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INFORMATION SHEET ON RECOVERY OF TARTRATES FROM GRAPE WASTES

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Bureau of Agricultural and Industrial Chemistry
Agricultural Research Administration
U. S. Department of Agriculture

During the past year the Western Regional Research Laboratory has conducted experiments designed to develop feasible and economical methods for the recovery of tartrates and other valuable constituents from grape wastes. It is planned to continue these researches as long as results obtained may warrant. Meanwhile workable and efficient processes have been devised for recovery of tartrates from pomace and brandy still slops.

I. Recovery of Tartrates from Still Slops

Tartrate occurs in brandy still slops as a very dilute solution and is accompanied by large amounts of extraneous materials, among which other acids and salts, pigments, and colloidal matter are especially important. To recover a product of high purity in satisfactory yield it is necessary to separate the tartar from undesired constituents and to concentrate it so that calcium tartrate can be precipitated without undue loss due to retention by the mother liquor.

Both ends can be attained through the use of synthetic anion exchangers placed in beds similar to filter beds. When still slop is passed through these exchangers under controlled conditions the tartrate remains affixed to them while most of the unwanted material passes through. When the exchanger bed has attained a capacity load, a solution of sodium chloride is passed through it to remove the tartar as sodium tartrate solution of about 5 percent concentration. At the same time the sodium chloride solution prepares the bed for another cycle. The action of the exchanger bed is complex but it is represented adequately by the diagrams of figure 1.

The process will yield calcium tartrate of excellent purity, and recovery will amount to 85 percent or more even in the case of dilute slops. The operation can be handled by one man with the necessary technical supervision and perhaps some help with the precipitations. Chemical reagent costs at present prices will amount to about 4 cents per pound of tartrate recovered. It is anticipated that further research will result in reduction of this figure.

Anion exchange materials are expensive and a substantial portion of the recovery costs will be chargeable to them. In the laboratory they have been carried through 100 exchange cycles of the type described herein and have suffered only minor diminution in efficiency. A recovery of about 4.6 pounds of tartaric acid per cubic foot of exchange material per cycle may be expected from "Amberlite IR-4", manufactured by the Resinous Products and Chemical Company, Washington Square, Philadelphia, Pennsylvania. Other exchange materials are manufactured by the Chemical Process Company, 58 Sutter Street, San Francisco, California, the Permutit Company, 330 West 42nd Street, New York, N. Y., Infilco Inc., 325 West 25th Place.

Chicago, Illinois, American Cyanamid & Chemical Corporation, 30 Rockefeller Plaza, New York, N. Y., and possibly others. 1/ The capacities of the various available materials vary rather widely.

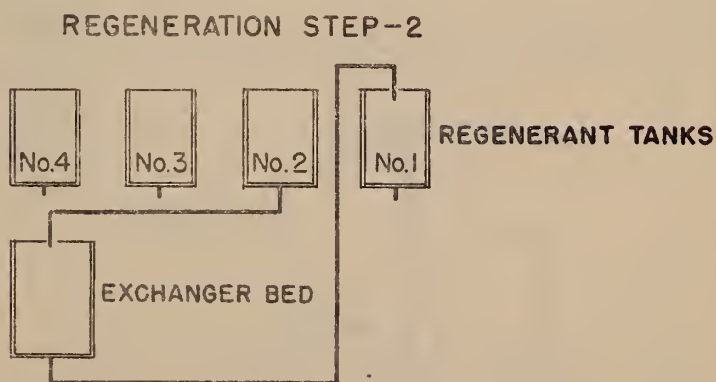
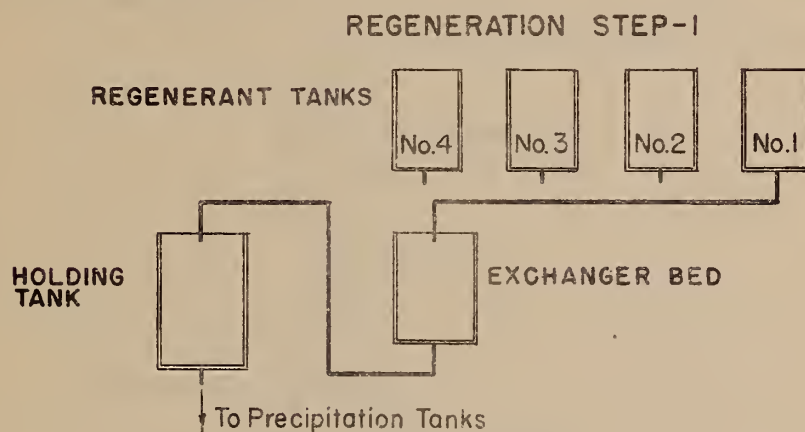
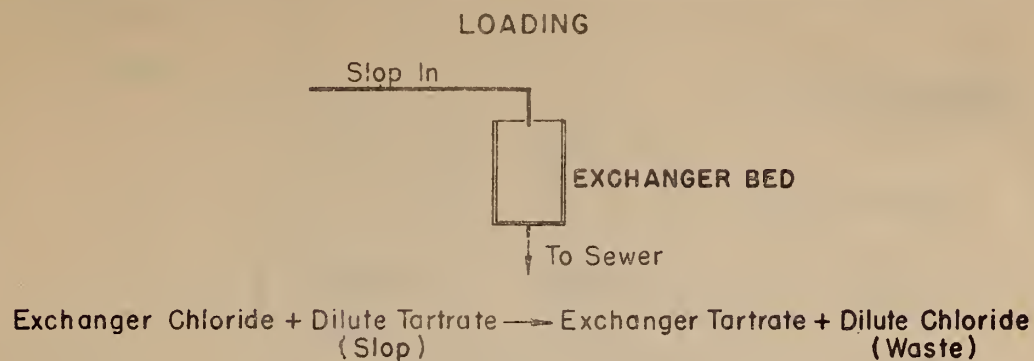
In operation the exchanger as received from the manufacturer is converted to the form of the hydrochloride by passing dilute hydrochloric acid through it. When the effluent changes from about neutral to strongly acid, still sloop is passed through the bed until it has become loaded; that is, until the tartrate content of the bed effluent, which will be negligible during most of the operation, has risen to perhaps 10 percent of that in the sloop. Sloop flow is then diverted to the second bed and the first regenerated with concurrent recovery of the tartrate. This is accomplished by flowing strong sodium chloride solution slowly through the bed.

The regenerant solution is maintained in four tanks (Fig. 2), the contents of which are flowed through the bed successively in counterflow fashion. After the operation has become established the first tank (strong tartrate liquor) will contain the highest concentration of tartrate (about 4 percent) and when the solution has passed through the freshly loaded bed and thus increased in tartrate concentration to about 5 percent it is pumped to a holding tank, from which it proceeds through a bed of activated carbon to the precipitation tank. The solution in the second tank (intermediate tartrate liquor) will, in its passage through the same bed, increase in tartrate concentration from about 2 to about 4 percent. It is pumped to tank No. 1, thus becoming strong tartrate liquor for the succeeding cycle. In the same way the solution in tanks No. 3 and No. 4 pass through the bed and become Nos. 2 (intermediate tartrate liquor) and 3 (weak tartrate liquor). Finally a similar volume of water is passed through the bed and pumped to tank No. 4, where salt is added to it in preparation for the next cycle.

The loading or sloop-flowing part of the operation is planned to require 3 hours with sloop of 0.3 percent tartar content (calculated as tartaric acid). The regeneration will require about 2 hours. The loading time will, of course, vary with the flow rate and tartar concentration of the sloop. If this concentration deviates substantially from 0.3 percent, or if the flow differs radically from that planned, the loading should be stopped when sloop equivalent to the bed capacity (about 4.6 pounds of tartaric acid per cubic foot in the case of Amberlite IR-4) has passed through. Wide variation in both factors can be tolerated without serious loss if the indicated precautions are carefully observed. A quick and accurate method for the determination of tartrates in still sloop is explained in a later section.

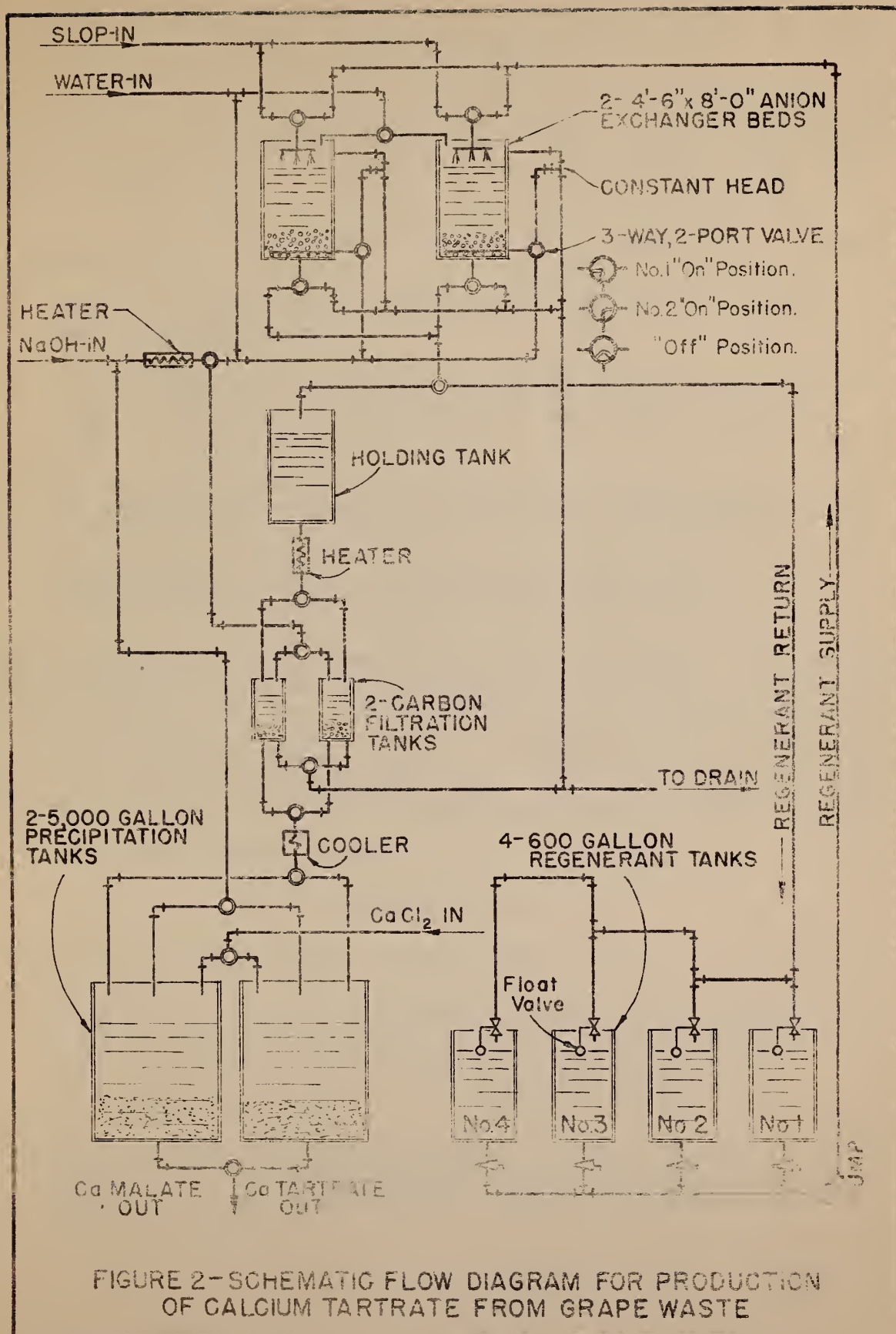
As mentioned above, the concentrated tartrate liquor is pumped to a holding tank, from which it proceeds to the precipitation tank through a bed of activated carbon. The carbon bed removes coloring matter and mucilaginous substances which would otherwise interfere with subsequent filtration and washing operations.

1/ The names of manufacturers mentioned throughout this report are supplied for convenience and not as specific recommendations.



Exchanger Tartrate + Conc. Chloride \longrightarrow Exchanger Chloride + Conc. Tartrate

FIGURE 1. DIAGRAMS AND EQUATIONS THAT REPRESENT THE ACTION OF AN EXCHANGER BED



Calcium tartrate is precipitated by adding calcium chloride solution in about 10 percent excess, after adjusting the pH to between 5 and 6 with sodium hydroxide. The precipitated calcium tartrate will be granular and practically white. It must be thoroughly washed to remove chlorides and dried quickly to avoid loss through bacterial action. These operations are greatly facilitated by the previous removal of interfering substances on the activated carbon. Mother liquor from the calcium tartrate precipitation is pumped to a second similar tank where malic acid may be recovered.

Certain precautions must be observed in carrying out the operations outlined. Of special importance are:

1. The slop must be cooled to below 85°F. before passage through the anion exchanger beds.
2. The slop should be reasonably clear before passage through the beds. In some cases it may be necessary to permit suspended matter to settle before treatment.
3. The exchanger beds must be thoroughly washed between cycles to remove adhering colloidal and suspended matter from them.
4. The calcium tartrate must be thoroughly washed to free it from chlorides and must be collected and dried in the shortest time possible in order to avoid bacterial action.

The accompanying sketch (Fig. 2) shows a suggested plant layout. Below are listed in detail the various operations for a plant having a still-slop flow of about 2,000 gallons per hour. For such a plant 64 cubic feet of exchanger will be required if "Amberlite IR-4" is used. This will be divided between two beds as indicated. Each of these beds is large enough to provide about 48 cubic feet of exchanger space (since the material swells nearly 50 percent in use) and a similar volume of head space to permit upflow washing to 100 percent bed expansion.

1. Flow slop through exchanger bed No. 1 for 3 hours.
2. Divert flow of slop to exchanger bed No. 2.
3. Drain exchanger bed No. 1 to bed level.
4. Pass water upflow through exchanger bed No. 1, at such a rate (200 gallons per minute should be available) that the bed is expanded 100 percent, until wash water is practically free from suspended particles (about 10 minutes); then drain the bed completely.
5. Pass contents of regenerant tank No. 1 (strong tartrate liquor) downflow through exchanger bed No. 1 at such a rate that about 20 minutes is required. Pump the effluent to the holding tank.

6. When the brine from regenerant tank No. 1 has reached bed level, start flow through the bed from regenerant tank No. 1. Start flow from tank No. 3 and from tank No. 4 in similar fashion. When brine from tank No. 4 has reached bed level, start water flowing at a similar rate.
7. When the required volume (360 gal.) of finished tartrate liquor has passed to the holding tank divert flow to regenerant tank No. 1 (strong tartrate liquor).
8. When 360 gallons has passed to regenerant tank No. 1, divert flow to regenerant tank No. 2 (intermediate tartrate liquor).
9. When 360 gallons has passed to regenerant tank No. 2, divert flow to regenerant tank No. 3 (weak tartrate liquor).
10. When 360 gallons has passed to regenerant tank No. 3, divert flow to regenerant tank No. 4 until 360 gallons (including salt; see No. 13 below) has been collected therein.
11. Wash the exchanger bed in the upflow direction (at such a rate that the bed is expanded 100 percent but little or no resin is washed out) until the wash water is free of suspended colloidal grape particles (about 10 minutes).
12. Drain the bed to exchanger level. It is now ready for the next cycle.
13. Dissolve 300 pounds of salt in the water contained in regenerant tank No. 4 and 150 pounds of salt in the solution contained in regenerant tank No. 1.

Calcium Tartrate Precipitation

Precipitations of tartrate are made periodically with any suitable time interval, and the size of precipitation equipment is gauged in accord with the interval chosen. If it is desired to precipitate once daily, each of the two tanks should have a capacity of about 5,000 gallons, which is somewhat greater than the expected requirement.

The decolorized solution is analyzed for its tartar content and the amount of calcium chloride required is calculated. This amount plus a 10 percent excess is dissolved in about twice its weight of water and the solution is added, with agitation, to the tank contents after the pH of the solution has been adjusted between 5 and 6 by adding strong sodium hydroxide solution, with thorough agitation.

When the precipitate has settled, the mother liquor is drawn off to a second tank for precipitation of calcium malate. The calcium tartrate is washed free of chlorides, collected, and dried quickly.

Research on recovery of malic acid is in progress and a procedure will be described as soon as the details have been worked out.

II. Recovery of Tartrates from Grape Pomace

Extraction of Pomace

Efficient and economical recovery of tartrates from grape pomace is primarily dependent on preparation of a clear aqueous extract of relatively high tartar concentration. Precipitation of calcium tartrate from too turbid solutions results in a product of unacceptable purity which, in addition, is difficult to accumulate, wash, and dry. Fining such extracts prior to tartrate precipitation improves the quality of the final product but involves losses through settling which may be very serious. A high tartar concentration in the extract is required since the liquors after precipitation of calcium tartrate may be expected to retain about 0.2 percent tartar (calculated as tartaric acid). This would represent a 20 percent loss if the original concentration were 1 percent or a 10 percent loss if it were 2 percent.

Experiments conducted at the Western Regional Research Laboratory have shown that both conditions are met if the process is carried out by hot counterflow extraction where there is no agitation of the pomace being processed. By such a procedure clear extracts having a tartaric acid content about 0.5 percent less than that of the pomace can be obtained. The last 0.2 to 0.3 percent of tartar in the pomace resists extraction and its recovery, though possible, would not justify the necessary additional expense required. Cloudy press liquor, which contains some tartar, is discarded for the same reason.

The operation should result in extraction of more than 80 percent of the tartar present in 2.5 percent pomace (wet basis) in condition for precipitation of calcium tartrate or crystallization of potassium bitartrate without further clarification. With pomace of higher tartar content the percentage obtained will of course be substantially higher.

One man should be able to handle the operation with some technical supervision and perhaps assistance in making precipitations. Additional labor would of course be required to transport the pomace to the equipment. It would be advantageous to carry out the operation as the pomace is produced. One handling would thus be avoided and there would be no opportunity for spoilage.

Three tanks of equal size for use as extractors are set up. Each has a filter bottom and a pump (for circulating extract through the charge), attached to the outlet, and is equipped with a closed steam heater. Condensation from open steam heaters would result in too great dilution of the extract and in agitation of the pomace with attendant turbidity of the extract. Each tank must have a capacity of about 1,000 gallons per ton of pomace to be extracted per hour.

The process involves three extractions for each charge of pomace, the first with relatively strong extract from the preceding extraction, the second with weaker extract of similar origin, and the third with water. It is carried out in accord with the accompanying tabulated procedure where the hour-by-hour operations are indicated in the horizontal columns. Nine hours' operation have been indicated. The tenth is exactly like the fourth; the eleventh like the fifth; and so on.

Counterflow Extraction Procedure for Recovery
of Tartaric Acid from Grape Pomace

Hour	Extractor No. 1	Extractor No. 2	Extractor No. 3
1	Extraction No. 1 (to ppt. tank)	Charge	--
2	Extraction No. 2 (to No. 2)	Charge	--
3	Extraction No. 3 (to No. 2)	Extraction No. 1 (to ppt. tank)	Charge
4	Empty	Extraction No. 2 (to No. 3)	Charge
5	Charge	Extraction No. 3 (to No. 3)	Extraction No. 1 (to ppt. tank)
6	Charge	Empty	Extraction No. 2 (to No. 1)
7	Extraction No. 1 (to ppt. tank)	Charge	Extraction No. 3 (to No. 1)
8	Extraction No. 2 (to No. 2)	Charge	Empty
9	Extraction No. 3 (to No. 3)	Extraction No. 1 (to ppt. tank)	Charge

The tenth hour is like the fourth, the eleventh like the fifth, and so on.

Extraction is to be carried out in 1900r. Volumes will be adjusted so that the finished extract contains 1.5 to 2.0 percent tartaric acid and the amount is circulated through one charge at as rapid a rate as possible. For pomace of 2.5 percent tartaric acid content, 220 gallons per ton will be suitable.

The extractors are of course charged continuously by a conveyor. They can be emptied through a door in the side to a second conveyor which removes spent pomace to the press or elsewhere. The extraction could well be preceded by an operation designed for alcohol recovery, especially if the pomace were heated during such a process.

Studies now under way indicate that malic acid may be obtainable from pomace. If it develops that the amount is sufficient to warrant recovery it is probable that the extract can be cooled to crystallize potassium bitartrate and malic acid can be recovered along with the remaining tartaric through the anion exchange procedure described for processing still slop. Until more is known on this point it will presumably be desirable to precipitate all the tartar as calcium tartrate.

Calcium Tartrate Precipitation

The precipitation of the calcium salt from the extract can be accomplished in a number of ways. The principal contingency to be avoided is destruction of tartar by the action of microorganisms and for information on this point consultation with the Fruit Products Division of the University of California is suggested.

Means for continuous precipitation of the tartar would be desirable and not too difficult to arrange. Perhaps the simplest procedure would be to place calcium chloride solution, in the amount anticipated to be required, in the precipitation tank before running in the extract. When extract is added, a part of the tartar will precipitate and the pH will fall to about 3, under which conditions the extract will probably not be attacked by microorganisms while cooling. When cool, the pH can be adjusted to about 4.5 (not over 5) with lime or caustic soda and the remaining tartrate thus precipitated. Calcium chloride is added at the beginning to avoid crystallization of potassium bitartrate during cooling.

It is of paramount importance to wash the calcium tartrate thoroughly and to dry it as quickly as possible.

III. Determination of Tartrates in Still Slop and in Pomace

Still slop.--The procedure for tartrate determination described here is based on that of Underhill and associates ^{2/} who measured the characteristic red color developed through interaction of sodium metavanadate and tartaric acid in dilute aqueous acetic acid solution. In the original procedure, colors were compared in Wessler tubes. It is simpler to make the estimation through photoelectric colorimetry, using the M-515 filter or one having a similar transmission band.

A concentration-transmission curve is first prepared from readings obtained with pure tartaric acid in the procedure described below. The range covered by the curve should be 1 to 5 mg. of tartaric acid per sample and the readings should be plotted on semilogarithmic paper.

^{2/} Underhill, F. P., Pateman, F. I., and Araujo, A. G., Jour. Pharmacology 43, 181 (1933).

1. Weigh 10 g. of tartaric acid or potassium bitartrate, colorless crystals, or white powder, in a 100-ml. volumetric flask. Dilute with about 50 ml. of water. The solution is decolorized by boiling for 2 to 4 minutes with about 0.2 gram of activated carbon B, diluted to 100 ml. and filtered through a No. 2 Whatman or similar paper. 4/

The colorimetric estimation is made as follows: To 0.5 ml. of decolorized acid contained in a 15-ml. graduated cylinder (stopped if used) or volumetric flask, add measured volume (not exceeding 20 ml.) of a decolorized and neutralized (pH 7) 0.1% solution containing from 1 to 5 mg. of tartrate, calculated as tartaric acid. Add the mixture to exactly 25 ml. when a graduated cylinder is used, and nearly the same volume when a volumetric flask is employed. Add 2 ml. of a 0.1% aqueous 50 percent sodium metavanadate solution 5/ and adjust the final volume to 25 ml. The solution is then set in a darkened place for 30 minutes for color development. When the color has developed to full intensity measure it with the colorimeter in the usual manner, using the M-45 filter. From the percentage of transmittance obtained, and comparison with the concentration-transmission curve for pure tartaric acid, the tartaric acid content of the original sample is readily computed.

Pomace.--For tartaric determination in grape pomace the procedure outlined above may be used, but the determination must be preceded by extraction. This is done as follows: A well-sized large sample (1 kg.) is successively quartered until the individual portions are between 50 and 75 grams. Weigh the sample accurately into a 2-liter Erlenmeyer and thoroughly disintegrate it (5 min.) with 250 ml. of water. Transfer the mass to a flask; add 50 ml. of concentrated hydrochloric acid, and boil 10 minutes. Then transfer to a 1-liter volumetric flask and dilute to volume. The solution is filtered and an aliquot (50 ml.) decolorized and neutralized. The procedure from this point is the same as that given above for still juice.

5/ Some samples of activated carbon have been found to absorb tartar hence the material should be tested with pure tartaric acid solutions prior to use.

6/ In some instances boiling is unnecessary but in other cases the filtrate is turbid regardless of the original pH, the amount of carbon, or the duration of the boiling period. This difficulty can be overcome by replacing the paper with a Gooch or an asbestos filter.

7/ The sodium metavanadate is conveniently dissolved in water at 50-60°C., made up nearly to volume, permitted to cool, and then filtered. In case of persistent turbidity, the fresh solution is permitted to stand for at least 24 hours, after which filtration is repeated. It is important to check the concentration-transmission curve at frequent intervals and especially so when fresh solutions of metavanadate are prepared.

8/ It has been observed that direct sunlight induces a bleaching of the color. This effect may not be noted unless the room is well lighted. However, it is clearly desirable to place the tubes in the dark for color development. Under these conditions, the color is very stable, showing no change over a period of 24 hours.

Note: Those interested in the processes are invited to visit the Eastern Regional Research Laboratory, Allegheny, Pa., to discuss details of plant design and operation.